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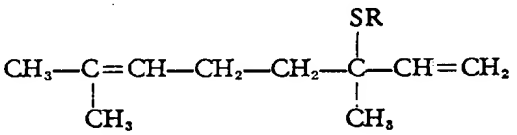
(54) NOVEL ODORANT AND/OR FLAVOURANT

(71) We, L. GIVAUDAN & CIE SOCIETE ANONYME, a Swiss Company of Vernier-Geneve, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention is concerned with a novel odorant and/or flavouring composition, with a process for the manufacture of this composition, and with a method for imparting an odour and/or flavour to materials.

The novel odorant and/or flavouring composition provided by the present invention contains, as an essential odour- and/or flavour-imparting ingredient, thiolinalool (3,7-dimethyl-3-mercapto-1,6-octadiene).

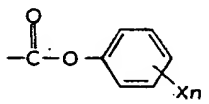
Thiolinalool may be manufactured by subjecting a compound of the general formula



(I)

wherein R represents a group which is cleavable by hydrolysis or hydrogenolysis, to hydrolysis or hydrogenolysis.

Examples of groups denoted by R are acyl groups such as lower alkanoyl groups (e.g. acetyl), aroyl groups (e.g. benzoyl), but especially groups of the general formula



(IIIa)

wherein X represents a halogen atom, preferably a chorine or bromine atom, a lower (C_1—C_6) alkyl group, preferably methyl, or a nitro group and n stands for zero or an integer of from 1 to 5, preferably 1 or 2.

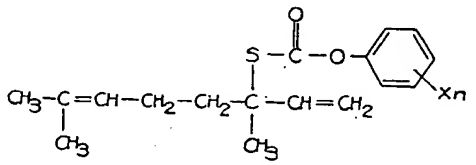
When n signifies an integer greater than 1, then the substituents denoted by X can be the same or different.

The hydrolytic cleavage of the group denoted by R to give the free thiol can be carried out according to methods known per se, conveniently by means of an alkali such as potassium hydroxide or sodium hydroxide in an aqueous or aqueous-alcoholic medium. According to a preferred mode of carrying out the hydrolysis, the mixture is heated to boiling under reflux. The hydrolysis can, however, also be carried out at lower temperatures (e.g. at room temperature).

The hydrogenolytic cleavage of the group denoted by R to give the free thiol can

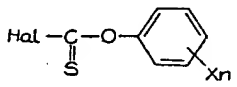
likewise be carried out according to methods known per se; for example, using lithium aluminium hydride in a solvent such as an ether (e.g. diethyl ether or tetrahydrofuran), conveniently at about room temperature. The hydrogenolysis is superior to the hydrolysis described hereinbefore insofar as less thiogeraniol is obtained as a byproduct.

The starting materials of formula I in which R represents a group of formula IIIa hereinbefore, i.e. compounds of the general formula



(II)

wherein X and n have the significance given earlier, can be prepared by reacting 3,7-dimethyl-2,6-octadien-1-ol, especially geraniol, with a compound of the general formula

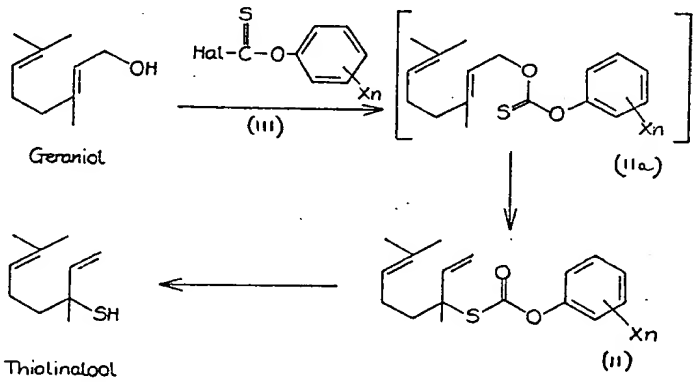


(III)

wherein Hal represents a chlorine or bromine atom and X and n have the significance given earlier,

conveniently in an anhydrous organic base, preferably pyridine, at a temperature between about 0°C and about 50°C, preferably between about 5° and 20°C.

A synopsis of the manufacture of thiolinalool from geraniol is illustrated in the following formula scheme in which X, n and Hal have the significance given earlier:



The product which is initially obtained from the reaction of a halide of formula III with geraniol can be denoted by formula IIa. This unisolated intermediate rearranges under the reaction conditions into a compound of formula II which is then hydrolysed or hydrogenolysed to thiolinalool.

The thiolinalool provided by this process is characterised by particular fresh, fruity odorant or flavouring properties. Of particular interest is a bitter grapefruit note and a roast note reminiscent of poultry which occurs with increasing concentration. The thiolinalool can accordingly be used, for example, for the perfuming or aromatisation of products such as cosmetics (soaps, salves, powders, etc.) or foodstuffs, condiments and drinks, whereby the thiolinalool is preferably not used alone but rather in the form of compositions which contain it together with other odorants or flavourings. Such odorant or flavouring compositions containing thiolinalool and the manufacture

of such compositions in a manner known per se (the addition of thiolinalool to known odorant or flavouring compositions or the admixture of thiolinalool with compounds suitable as ingredients of odorant or flavouring compositions) form part of the present invention. The content of thiolinalool in such compositions can vary within very wide limits (e.g. between about 10^{-7} and about 5 wt.%).

The following Examples 1 and 2 illustrate the manufacture of thiolinalool.

Example 1

a) 11 g (0.0715 mol) of geraniol are dissolved in 20 ml of pyridine and cooled to +5°C in an ice-bath under nitrogen. 12.1 g (0.065 mol) of p-tolylthionecarboxylic acid chloride are added dropwise during 30 minutes with vigorous stirring, whereby the temperature does not rise above 12°C. The mixture is subsequently stirred for a further 2 hours at room temperature, a brown-red colour setting in. After dilution with 500 ml of ether, the solution is washed in a separating funnel twice with 100 ml of 2-N aqueous sodium hydroxide each time, twice with 100 ml of 2-N aqueous hydrochloric acid each time and three times with 250 ml of saturated aqueous sodium chloride solution each time. The organic phase is dried over sodium sulphate and concentrated under a vacuum at 50°C. The residue (19.8 g) is distilled under a high vacuum, there being obtained, as the fore-run, unreacted geraniol and, as the main fraction (boiling point 138°C/0.06 mmHg), the desired S-linalyl-O-p-tolyl-thiol-carbonate (9.34 g). The UV/IR/NMR and MS spectra agree with the postulated structure (see formula II in which n stands for 1 and X represents p-CH_3).

NMR:	1.62+1.67 ppm	9H	*IR*:	1730 cm^{-1}, 1510 cm^{-1}
	1.85−2.2 ppm	4H		
	2.32 ppm	3H		
	5.0 −5.4 ppm	3H		
	5.85−6.4 ppm	1H		
	7.0 −7.3 ppm	4H		

b) A suspension of 400 mg (0.0105 mol) of lithium aluminium hydride in 25 ml of absolute ether is cooled to 5°C under nitrogen. 2 g (0.0066 mol) of S-linalyl-O-p-tolyl-thiolcarbonate dissolved in 25 ml of ether are added dropwise at this temperature over a period of 5 minutes with stirring. The mixture is then stirred for 18 hours at room temperature. After the addition of 100 ml of saturated aqueous sodium bicarbonate solution, the organic phase is washed a further three times with 100 ml of saturated aqueous sodium chloride solution each time, dried over sodium sulphate and concentrated under a vacuum at 50°C. According to gas-chromatographic analysis, the residue (1.81 g) consists of thiolinalool and p-cresol to more than 90%. These two compounds are separated by column chromatography on Kieselgel using a hexane/ether mixture (19:1). The thiolinalool fractions which are obtained initially are combined and the solvent is distilled off. The residue (0.78 g) is distilled in a bulb-tube under a water-jet vacuum (boiling point 96°C/8 mmHg). There are obtained 570 mg of thiolinalool, the UV/IR/MS and NMR spectra of which agree with the postulated structure.

NMR:	1.47 ppm	3H	*IR*:	2600 cm^{-1},	*MS*: M^+ 170,
	1.62+1.7+1.76 ppm	6H		1640 cm^{-1}	m/e 155, 136,
	1.5 −2.35 ppm	5H			121, 93, 81,
	4.85−5.3 ppm	3H			80, 69, 59, 55
	5.75−6.3 ppm	1H			

Example 2

a) 1 g of S - linalyl - O - 4 - chlorophenylthiolcarbonate is dissolved in 10 ml of methanol and treated with 10 ml of a 10% aqueous potassium hydroxide solution. The mixture is heated under reflux for 2 hours. After cooling to room temperature, 100 ml of ether are added, the organic phase is washed three times with 50 ml of saturated aqueous sodium chloride solution each time, dried over sodium sulphate and concentrated under a vacuum at 50°C. The residue (0.88 g) consists of thiolinalool, thiogeraniol and p-chlorophenol. The latter is separated from the mercaptans by column chromatography on Kieselgel using a hexane/ether mixture (19:1). The thiolinalool and thiogeraniol fractions are combined and the solvent is distilled off. The residue (0.27 g) is distilled in a bulb-tube (boiling point 100°C/8 mmHg). According to gas-chromatographic analysis, the dis-

tillate (147 mg) consists of approximately 30% of thiolinalool and of approximately 70% of thiogeraniol.

b) The S - linalyl - O - 4 - chlorophenylthiolcarbonate can be prepared from geraniol and 4-chlorophenylthionecarboxylic acid chloride in an analogous manner to that described in part a) of Example 1.

The following Examples illustrate typical compositions containing the thiolinalool provided by the present invention:

Example A

Perfume composition (lavender type)	Parts by weight
Patchouli oil	5
Coumarin	5
Rosemary oil Spanish	30
Ethyl amyl ketone 10% in diethylphthalate	30
p-Tertiarybutyl-cyclohexyl acetate	30
Linalyl acetate	100
Bergamotte oil synthetic	100
Lavandin oil	100
Lavender oil	100
Lavender oil cult	500
Carbitol (trade mark for diethyleneglycolmonomethyl ether)	100
	1000

When 0.05—0.1 g of thiolinalool is added to 1000 g of the foregoing lavender composition then there is immediately observed a very positive alteration of the odour. In particular, an improved harsh-herby note now appears. The diffusion of the odorant composition is, moreover, distinctly improved.

Example B

a)

Citrus aroma	Parts by weight
Methylheptenone	0.5
α-Terpineol	1.0
Linalool	1.0
n-Decylaldehyde	1.5
Octylaldehyde	1.0
Acetic acid geranyl ester	1.5
Citral	60
Citrus oil	100
Propyleneglycol	833.5
	1000

After replacement of the linalool in the foregoing composition by 10 parts of a 1% alcoholic solution of thiolinalool, there can be immediately observed a distinctly perceptible, desirable improvement of the required citrus peel notes.

b)

Orange aroma	Parts by weight
Capricaldehyde 10% in ethanol	2.5
Propionic acid geranyl ester 10% in ethanol	7.5
Orange oil American	990
	1000

After the addition of 5 parts of a 1% solution of thiolinalool to the foregoing aroma, there is immediately observed a distinct improvement of the fruit-like aroma of the flavouring composition.

Aromas a and b hereinbefore can be used, in particular, in confectionery, but also in the production of yoghurts, lemonades, etc.

WHAT WE CLAIM IS:—

1. An odorant and/or flavouring composition which contains thiolinalool as an essential odour- and/or flavour-imparting ingredient.

2. A process for the manufacture of an odorant and/or flavouring composition, which process comprises adding thiolinalool to known odorant and/or flavouring compositions or mixing thiolinalool with compounds suitable as ingredients of odorant and/or flavouring compositions or with mixtures of such compounds.

3. A method of imparting an odour and/or flavour to materials, which method comprises applying to said materials or incorporating therein an odour- and/or flavour-imparting amount of thiolinalool or an odorant- and/or flavouring composition as claimed in claim 1.

4. A method as claimed in claim 3, substantially as described in Example A or Example B.

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